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Application of low-grade recyclate to enhance reactive toughening of poly(ethylene terephthalate)

Katalin Bocz[a,*], Ferenc Ronkay[b,c], Kata Enikő Decsov[a], Béla Molnár[b,c], György Marosi[a]

[a] Department of Organic Chemistry and Technology, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary
[b] Imsys Ltd, Material Testing Laboratory, Mozaik Street 14/A., H-1033 Budapest, Hungary
[c] Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary

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ABSTRACT

This paper presents a new recognition in reactive toughening of poly(ethylene terephthalate) (PET), namely the major effect of the molecular weight of PET on the evolution of the compatibilization and crosslinking reactions with ethylene–butyl acrylate-glycidyl methacrylate (EBA-GMA) type reactive terpolymer, and thus indirectly on its toughening efficiency. It was found that the use of highly degraded recycled PET (rPET) grades, due to the available larger number of reactive functional end groups and increased mobility of the decreased-molecular-weight chains, multiplies the impact strength of the product compared to that of original PET (oPET) with identical EBA-GMA contents. The evinced noticeable difference between the toughening behaviour of rPET and oPET is explained by morphological and interfacial factors and connected to differences in rheological behaviour as well. The reactive oligomeric rPET macromolecules form a Toughening Enhancer Interphase (TEI) around the dispersed particles. Based on systematic analyses, conclusions were drawn regarding the quality, i.e. optimal intrinsic viscosity (IV) range, and quantity of rPET to be used to obtain high-impact-strength PET blends (notched Izod impact strength higher than 40 kJ/m^2) with optimised mechanical properties, being suitable even for injection moulding applications, at significantly lower terpolymer contents (10.0–12.5 wt%) than expected. Besides, the proposed new way of utilisation of PET recyclates, especially the unmarketable highly degraded fractions, is believed to give a new driving force in PET recycling.

1. Introduction

The global production of poly(ethylene terephthalate) (PET) is increasing every year, exceeding 30 million tonnes in 2017 [1]. As PET plays a prominent role in the field of the production of short-life packaging materials [2], the quantity of discarded PET is also rapidly growing. Recycling of PET waste by producing durable products targeting other industries such as electrical and electronics, automotive, etc. [3–5] would mean an important move towards a more circular economy [6,7]. In these industries, injection moulding is the most common plastic processing method, which is the greatest barrier to using PET, the injection mouldings of which are especially brittle and notch sensitive [8–10]. Furthermore, the inevitable degradation (thermal and hydrolytic due to the large number of unstable ester groups) during the thermal reprocessing of PET flakes reduces the average molecular weight and increases the rate of crystallization and thus the amount of crystalline fraction in the recycled product [8,11–14] accompanied with even lower impact resistance [15,16].

Blending with elastic polymers is a widely applied solution for toughening of brittle polymers [17–19]. In general, distributed elastic component can increase toughness in two ways: by forming micro-cracks (crazing) and by shear banding (shear yielding) [19]. The function of the dispersed rubber particles is two-fold [20]: on the one hand, they need to generate a local stress concentration, on the other hand, they need to void (cavitate or debond) and thus alter the stress state in the surrounding matrix material allowing an overall deformation mechanism to take place [21]. The nature of the modified deformation mechanism is highly dependant on the composition and structure of the mixture influenced mainly by the type [22], the ratio and the size of the rubber phase [23–27], the distance between the distributed particles [19–21,24,28],

* Corresponding author.
E-mail address: kbocz@mail.bme.hu (K. Bocz).

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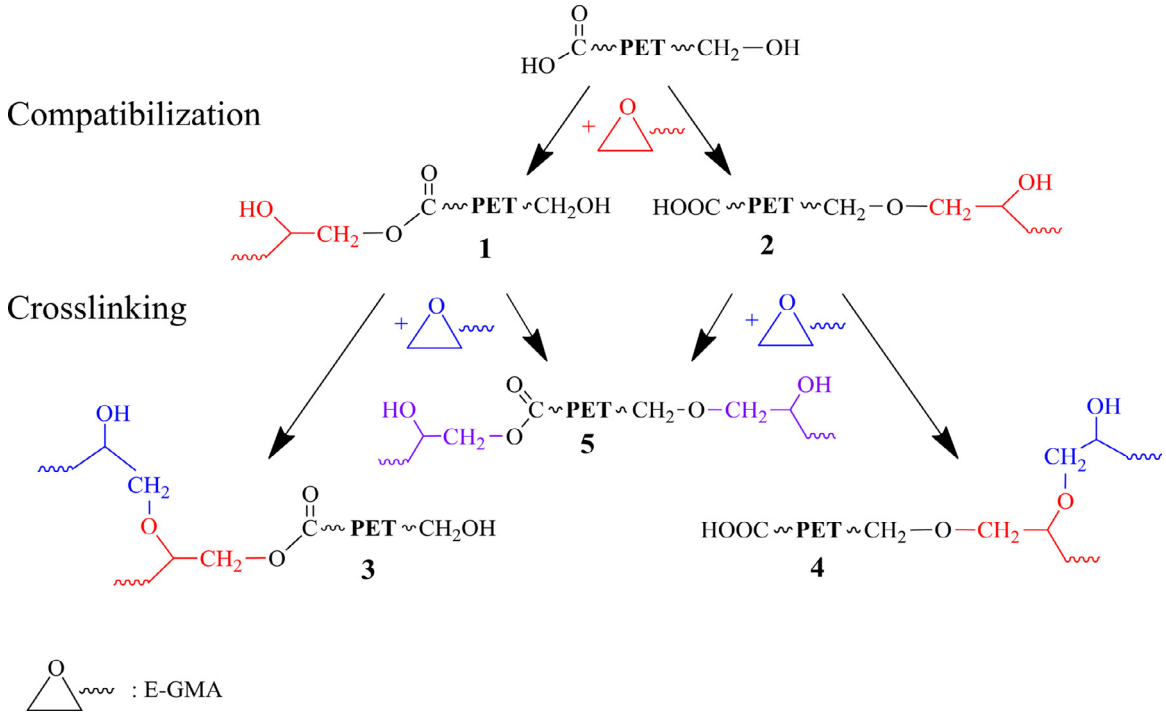

Fig. 1. Schematic illustration of compatibilisation and crosslinking reactions of PET/E-GMA blends.

the interfacial effects, and the entanglement of the matrix polymer [19,21,29]. Some studies pointed out that the rubber particle size generated during processing and the critical interparticle distance are also a function of the molecular weight of the matrix [30–32]. It was found that with higher molecular weight the range of rubber particle sizes for effective toughening is wider and consequently higher levels of toughness can be achieved.

Since the hydroxyl and carboxyl functional groups of thermoplastic polyesters are highly polar while the elastomeric phase is generally apolar due to the lack of functional groups, interfacial tension is high which makes reactive compatibilization necessary [21,33–35]. This may be accomplished by the use of functionalized elastomers which provide a direct link between the matrix and the distributed component, or by a third component compatible with at least one component and that may react with the functional group of the other components [33]. *Loyens* and *Groeninckx* reported three studies on enhancing the impact resistance of PET with reactive compatibilization [18,21,33]. In their experiments, ethylene-propylene rubber grafted with glycidyl methacrylate (EPR-g-GMA) and ethylene–glycidyl methacrylate (E-GMA) copolymers with various GMA contents were prepared by reactive extrusion. Similarly to other researchers [17,35–37], they found that during melt blending, GMA reacts with the hydroxyl and carboxyl groups of PET forming graft copolymers at the interface and reduces the diameter of the distributed rubber particles. This was explained by the strong interfacial interaction between these phases, which inhibits interface mobility, thus suppressing the interaction and coalescence of the dispersed droplets. It was found that the E-GMA after the compatibilization is able to perform a (hydroxyl/epoxide) second crosslinking [33,38,39], the proposed reaction schemes are illustrated in Fig. 1. These interfacial reactions affect the resulting structure since the distributed component became more viscous and less deformable, droplet breakup is prevented, giving rise to non-spherical, rough morphologies and increased torque responses [33,40].

Many studies focused on the compatibilization and crosslinking of elastomeric ethylene–butyl acrylate-glycidyl methacrylate terpolymer (EBA-GMA) when distributed in a polyester [34,35,40,41]. *Liu* et al. evinced an outstanding (35-fold) improvement in the notched Izod impact strength when 15 wt% EBA-GMA and 5 wt% zinc ionomer were used at high processing temperatures, while the tensile strength and modulus did not change significantly [18]. *Zong* et al. [36] also used EBA-GMA for toughening of PET with an intrinsic viscosity (IV) value of 0.90 dl/g. At 20 wt% EBA-GMA content, a 26-fold increase of impact strength was achieved. Based on the increased processing pressure noticed during extrusion of this blend, a chemical reaction between the PET chains and the epoxy groups of EBA-GMA was assumed. *Cheng* et al. [42] improved the toughness of glass fibre reinforced recycled PET (with IV value of 0.65 dl/g) composites by adding EBA-GMA elastomeric terpolymer. By systematically increasing the terpolymer loading from 0 to 16 wt%, an almost linear increase in impact strength was found.

Nevertheless, in the research works conducted towards the reactive toughening of polyesters, the potential influence of the molecular weight of the matrix material on the evolution of the compatibilization and crosslinking reactions of EBA-GMA and indirectly on the toughening efficiency has not yet been investigated. Our main goal is to develop high-performance secondary materials with reduced additive content offering an ecologically and economically preferable alternative to primary plastics. For this purpose, unmarketable, highly degraded PET grades, having an increased number of functional end groups and increased molecular mobility, are proposed to be utilised as mediators to enhance the toughening efficiency of EBA-GMA.

2. Materials and methods

2.1. Materials

As original material, NeoPET 80 (Neo Group, Lithuania) type PET (**oPET**) with an intrinsic viscosity (IV) value of 0.80 ± 0.02 dl/g (M_w= 27 400 g/mol as measured by GPC) and a bulk density (indicating the weight of the material, in pellet or flake form, per unit volume) of 0.97 g/cm^3 was used. Recycled PET flakes (re-

ceived from JP Pack, Hungary) with an IV of 0.56 ± 0.03 dl/g (M_w = 16 900 g/mol as measured by GPC) were used as low-grade PET (**rPET**) material. The rPET flakes originate from the food packaging industry, where sheets were extruded and thermoformed from 100% bottle-grade recyclate and the scrap remained from the sheet production after cutting of parts (trays) was ground to obtain flakes to be recycled. The bulk density of the recycled material was measured to be 0.50 g/cm^3 (d_{50} = 2.0 mm; d_{90} = 3.6 mm). The number of total end groups, calculated according to Eq. (1) [43], is estimated to be 75 μeqiv/g and 116 μeqiv/g for the oPET and rPET, respectively.

$$Total\ end\ groups = \frac{57.46}{IV^{1.205}} \quad (1)$$

Elvaloy PTW (DuPont, USA) type ***EBA-GMA*** with 5.25 wt% GMA content and a melting point of 72 °C was used as reactive toughening agent.

2.2. Sample preparation

Compounding was performed with an LTE 26–48 (Labtech Scientific, Thailand) type twin-screw extruder. Before extrusion, PET materials were dried at 160 °C for 4 h, while EBA-GMA was dried at 70 °C for 4 h. Zone temperatures between the hopper and the die were between 245 °C and 270 °C and the screw speed was 20 1/min.

60 mm × 60 mm × 2 mm plaque specimens were injection moulded using a 50 MEtII (Mitsubishi, Japan) electric injection moulding machine. Zone temperatures varied from 260 °C to 275 °C, and mould temperature was 60 °C. Injection speed was 80 mm/s, holding pressure was 30 MPa, and back pressure was 2 MPa. Materials were dried at 160 °C for 4 h before injection moulding.

2.3. Methods

Melt flow index (MFI) measurements were carried out using a LMFI-2LENNCN (Dynisco, USA) MFI tester, according to ISO 1133 standard. The applied mass was 2.16 kg, the temperature was 260 °C.

IV measurements were done by RPV-1 (PSL Rheotek, USA) automatic solution viscometer according to ASTM D4603 standard. The IV values were measured at 30 °C in a 60/40 wt mixture of phenol/tetrachloroethane solvent with a concentration of 0.5 g/dl.

Gel permeation chromatography (GPC) analysis was performed on the PET raw materials with different IV values to determine the molecular weight distribution and average molecular weights. 1,1,1,3,3,3-Hexafluoro-2-propanol (hexafluoroisopropanol, HFIP) eluent was used for the measurements. The GPC instrument was equipped with a Jetstream 2 plus thermostat, a Waters HPLC Pump 515, an HFIP-806 M column, and a Jasco RI-4035 differential refractometer detector. The measurement temperature was 40 °C, the flow rate was 0.5 mL/min, and the HFIP eluent contained 5 mM Na-trifluoroacetate. Evaluation of the chromatograms was performed by using PSS WinGPC software based on calibration with narrow molecular weight distribution poly(methyl methacrylate) standards.

Melt rheology under dynamical shear was investigated using an AR 2000 type rotational rheometer (TA Instruments, New Castle, DE, USA) with 25 mm diameter parallel-plate geometry. Dynamic frequency sweep tests were performed at 260 °C to measure the complex shear viscosity over a frequency range of 0.1–100 Hz under controlled strain of 1%.

Torque measurements during melt mixing were performed in a Brabender Plasti-Corder internal mixer. Equally 60 g of materials had been weighted according to the compositions, dry-mixed and then added in the 50 cm^3 mixing chamber at 260 °C with rotors rotating at 50 rpm and mixed for 10 min. The variation of torque moment during melt mixing was continuously recorded.

Structure of different blends was characterized by EVO MA15 (Zeiss, Germany) scanning electron microscope (SEM), after selective extraction of EBA-GMA additive. For this, injection moulded specimens were cut, embedded in epoxy resin, polished, and after that, the embedded specimens were immersed in toluene (Molar Chemicals Kft, Hungary) for 6 h at room temperature. For SEM analysis 5 nm gold coating was applied.

The crystalline phase was analysed by DSC 131EVO (Setaram, France) differential scanning calorimeter. 10 °C/min heating and cooling rate were applied in the 30–300 °C temperature range. The crystal melting enthalpy was measured to calculate the crystallinity of each material according to Eq. (2):

$$CRF_M = \frac{\Delta h_M}{\Delta h_0 (1 - r_{EBA-GMA})} 100\%, \quad (2)$$

where CRF_M [%] is the calculated crystallinity from the melting peak; Δh_M [J/g] is the measured mass-specific heat flow during the melting (area of the melting peak), Δh_0 [J/g] is the mass-specific enthalpy of the 100% crystalline PET (140.1 J/g); $r_{EBA-GMA}$ [-] is the ratio of the EBA-GMA additive. The crystallinity calculated from the cold crystallization enthalpy was given according to Eq. (3):

$$CRF_{CC} = \frac{\Delta h_{CC}}{\Delta h_0 (1 - r_{EBA-GMA})} 100\%, \quad (3)$$

where CRF_M [%] is the relative crystallinity calculated from the cold crystallization peak; Δh_{CC} [J/g] is the measured mass-specific heat flow during the cold crystallization (area of the cold crystallization peak). The initial crystallinity of the samples was calculated by Eq. (4):

$$CRF_0 = CRF_M - CRF_{CC}, \quad (4)$$

where CRF_0 [%] is the initial crystallinity of the measured sample.

Izod impact tests were carried out by 5113.10.01 type (Zwick, Germany) impact tester at room temperature. Pendulum energy was 5.4 J. Tests were performed based on ISO 179–1 standard but using double-notched specimens (type 3 with notch type A) to ensure complete fracture in all cases.

Flexural tests were performed using an L3369 (Instron, USA) universal mechanical tester according to ISO 178 standard. Span was 32 mm, crosshead speeds were 1 mm/min for modulus determination, and 10 mm/min for other calculations, respectively. Video extensometer was used for displacement measurement.

3. Results and discussion

3.1. Reactive toughening of oPET and rPET with EBA-GMA

Reactive toughening of oPET and rPET was investigated by preparing two-component blends with increasing EBA-GMA contents ranging from 0 to 20 wt% with 5 wt% steps. The evolution of the double-notched Izod impact strength of the two types of injection-moulded specimens is compared in Fig. 2. Accordingly, with increasing EBA-GMA content a distinctive brittle-ductile transition can be seen in both matrices, reaching more than ten-fold increase in the impact strength. This transition appears at much lower EBA-GMA content (between 5 and 10 wt%) when recycled matrix material (rPET) is used than in the case of the oPET matrix (between 15 and 20 wt% EBA-GMA content). In other words, about 50 wt% less reactive compatibilizer suffices to achieve a drastic increase in the impact resistance of rPET than necessitated in oPET. In the literature, 20–25 wt% of EBA-GMA type compatibilizer was commonly required to reach the brittle-ductile transition of oPET [10,18,36]. Nevertheless, *Kunimune* et al. [44] achieved

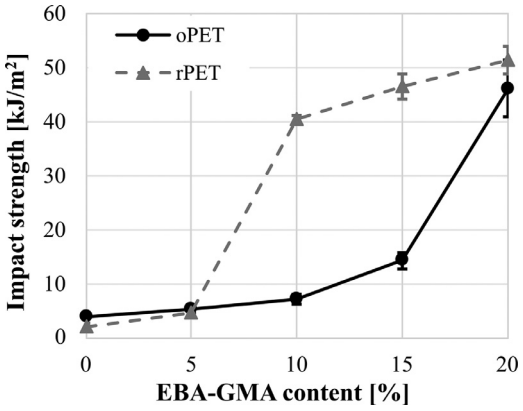

Fig. 2. Izod impact strength as a function of EBA-GMA content in oPET and rPET matrices.

drastic enhancement in the toughness of recycled PET with as low as 13.5 wt% E-GMA additive. Based on these results, and in accordance with our finding, the influence of the polymer matrix on the toughening efficiency of the reactive compatibilizer can be anticipated, still, it has not yet been investigated.

Based on the results in Fig. 2 one can assume that the observed difference between the toughening behaviour of oPET and rPET must be related to morphological and/or interfacial factors. In order to support the assumption, the structure of the samples was investigated. SEM micrographs taken from the selectively extracted cross-sections of the two types of binary blends with 10 and 20 wt% EBA-GMA contents are shown in Fig. 3. It can be seen that in the case of oPET the size of the dispersed droplets are larger and their shape is more irregular than in the case of rPET, where traces of noticeably smaller (even submicronic) and more spherical EBA-GMA particles are visible. Irregularly shaped EBA-GMA particles are assumed to be formed as a result of crosslinking reactions taking place in the dispersed phase, as parts fixed with crosslinks inhibit the achievement of the ideal spherical surface area/volume ratio [33,40]. According to Fig. 3b, 10% EBA-GMA has in contrast a homogeneous and stable dispersion in the rPET matrix, resulting in a small interparticle distance, which explains the sharp increase in toughness. This is consistent with the findings of *Wu* et al. [24] that reducing the distance between the dispersed phases below a critical value allows shock energy to be absorbed by extensive shear yielding, as also indicated by the fraction surface of this binary blend (Fig. 4b). In the case of oPET, however, the dispersion is only refined at 20% EBA-GMA content (Fig. 3c) to an extent that allows a sharp increase in impact toughness. At lower EBA-GMA content brittle failure characteristics can be identified (Fig. 4a).

The morphology development during melt-blending was followed by torque measurements performed in a Brabender internal mixer operated at 260 °C and 50 rpm. It has to be noted that at this elevated temperature the EBA-GMA is highly reactive [40], but not only the compatibilization reaction at the PET/EBA-GMA interface is accelerated but the terpolymer becomes more susceptible to crosslinking as well. The torque change with mixing time as recorded during the melt-blending of oPET and rPET with increasing amount of EBA-GMA are shown in Fig. 5a and b, respectively. The first peak of the torque response is attributed to the melting of the major polymer component, which appears noticeably earlier and is accompanied with lower torque increment in the case of rPET. This phenomenon is mainly due to the difference between the friction and melting characteristics of the round oPET pellets and the rPET flakes. Then, a second peak or shoulder displays in the torque response as a function of mixing time (mostly visible in the case of the blends with 10% or higher EBA-GMA contents) accompanied with increased resulting torque values, clearly indicating the occurrence of compatibilization reactions between the carboxyl and/or hydroxyl end groups of PET and the epoxide function of EBA-GMA [33] (Fig. 1). The terpolymer EBA-GMA itself is a flexible polymer and possesses a high sensitivity of melt viscosity to shear rate [45]. At high shear rates, applied during processing (both in the internal mixer and in the twin-screw extruder), the apparent viscosity of the elastomeric terpolymer is comparable with that of rPET (and noticeably lower than that of oPET), as it can be seen in Fig. 6, still, the equilibrium torque values of both types of the blends continued to increase with increasing EBA-GMA contents. Thus, the increase of the blend viscosity (equilibrium torque) indicates a chemical reaction taking place between the blend components. In Fig. 6, the experimentally measured torque values, recorded after 6 min of mixing, are compared to those of theoretically expected torque values, calculated from the rule of mixing of the equilibrium torque values of the individual blend components (without any reaction). It can be seen that the difference from the theoretically expected values is greater (both in absolute and in relative quantification) in case of the oPET based blends, especially at higher EBA-GMA contents. The observed high torque values confirmed the occurrence of other reactions additional to compatibilization, namely crosslinking of the terpolymer (Fig. 1). Significant crosslinking, also indicated by the broad increment of the torque curve, was revealed from 15% EBA-GMA content in the case of oPET matrix (Fig. 5a), while in the case of the rPET matrix, only with the highest (20%) EBA-GMA content (Fig. 5b). This difference is proposed to be attributed to the fact that at a fixed EBA-GMA concentration, the shorter chains of rPET have more functional groups with increased carboxyl to hydroxyl ratio [46,47] accompanied with increased mobility to react with the epoxide function of EBA-GMA. (It is known that both carboxylic and hydroxyl groups can react with an epoxy group, with the former being more reactive [48]). In contrast, in the oPET matrix more epoxy groups of EBA-GMA remain unreacted leading to a higher degree of crosslinking and in less deformable and non-spherical dispersed phase morphologies as a consequence (Fig. 4).

The rheological properties of the two types of blends were further investigated. In Fig. 7, the complex viscosity of 10% EBA-GMA containing oPET and rPET blends, as a function of frequency, are compared in a log-log plot. At higher shear rates ($10\ 1/s <$) the complex viscosity of the oPET based blend is higher than that of the rPET based blend with identical 10% EBA-GMA content, which is in connection with the inherent difference in the molecular weight and mobility of the two PET systems. The system containing rPET shows pronounced shear-thinning because the shorter chain polymer or oligomer macromolecules bonded to the dispersed particles (acting as a self-compatibilizing interphase) restrict the independent mobility of the particles at a low shear rate, while the interaction between the interphases is gradually released at higher shear rate thus the free-flowing is less restricted. Such interacting interphase is missing around the particles (of larger particle size) forming the dispersion in the oPET system thus the structure changes only moderately with the increasing shear rate resulting in lower value of shear thinning. In the range of lower shear rates (< 1 1/s), the viscosity curve of rPET prevails over that of the oPET + 10% EBA-GMA blend, which is further evidence for the more effective rPET/EBA-GMA bonding, which significantly increases the hydrodynamic diameter of the resulting copolymer and by this means clearly leads to an increase in viscosity. The interphase formed around the dispersed terpolymer particles creates the significantly increased impact resistance thus we call it Toughening Enhancer Interphase (TEI).

Further information on the phase structure of the produced blends can be obtained by analysing their thermal behaviour. The results of the DSC measurements are shown in Table 1. The glass

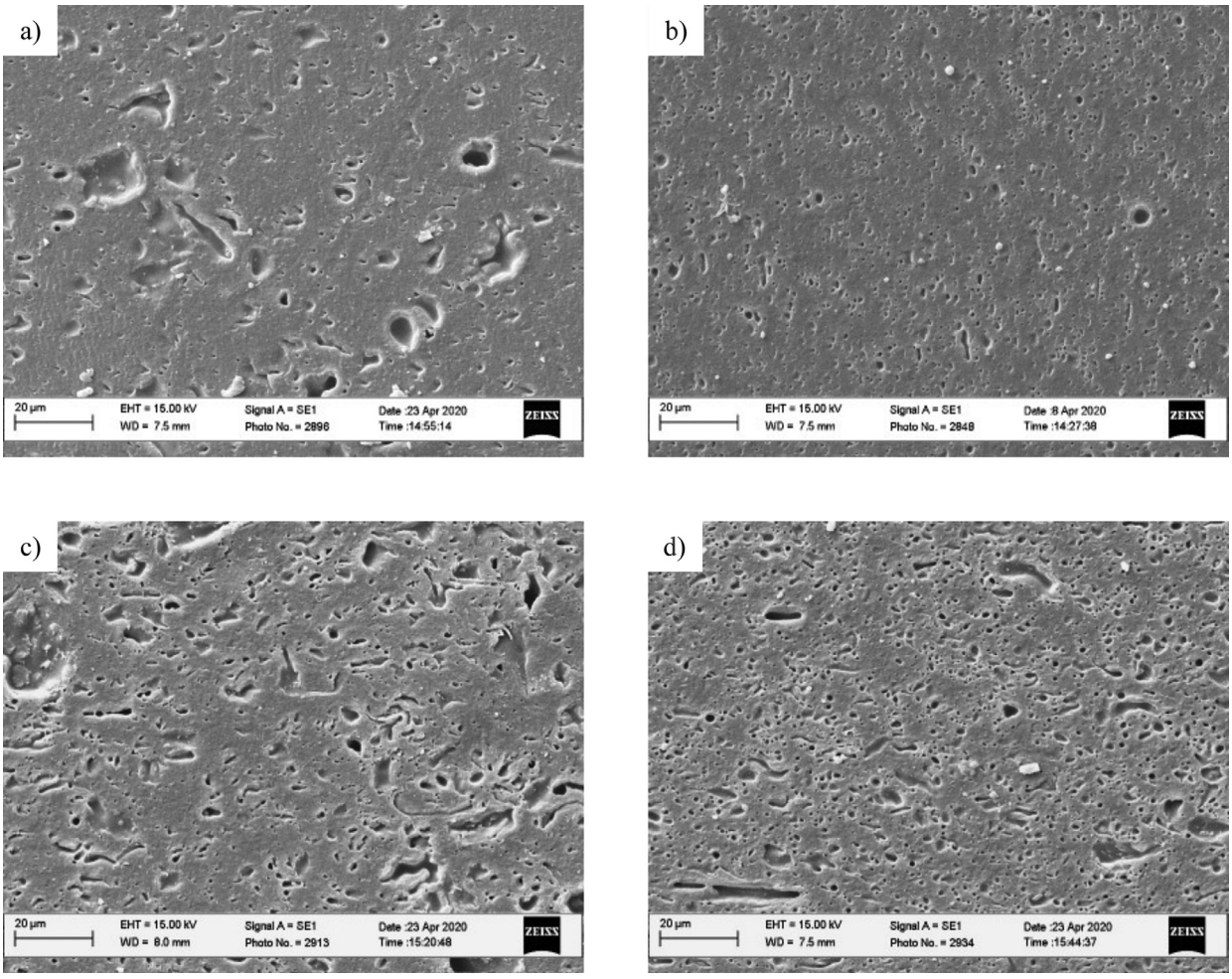

Fig. 3. SEM images of the polished cross-section of the blends after selective dissolution of the EBA-GMA phase: a) oPET + 10% EBA-GMA; b) rPET + 10% EBA-GMA; c) oPET + 20% EBA-GMA; d) rPET + 20% EBA-GMA.

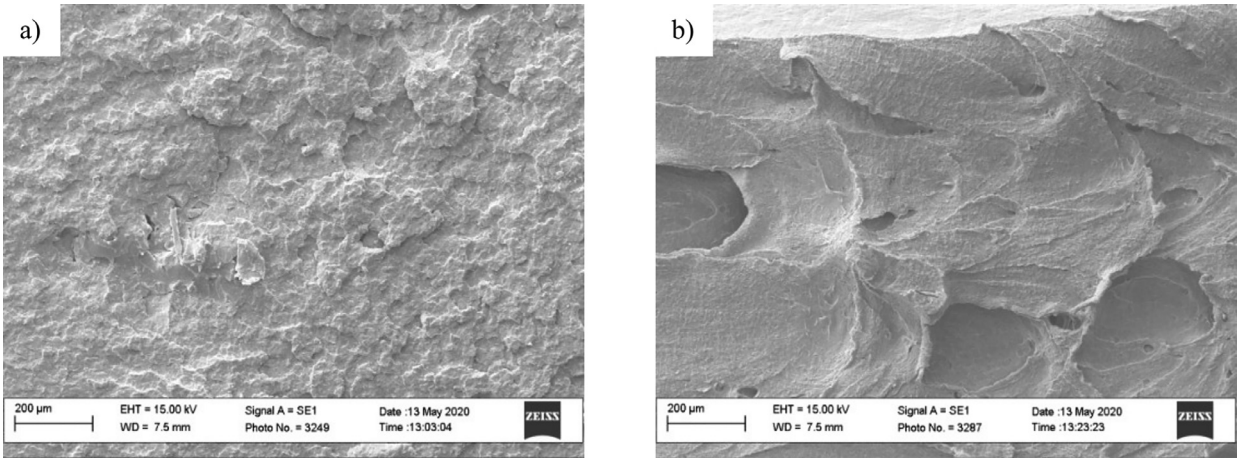

Fig. 4. SEM images of the fracture surface of (a) oPET + 10% EBA-GMA and (b) rPET + 10% EBA-GMA.

transition temperature did not change significantly, it ranges between 74.2–77.2 °C for both oPET and rPET matrices, independently of EBA-GMA content. Comparing the initial crystallinity of the two matrix materials, it can be concluded that although both groups show a decreasing trend with increasing EBA-GMA content (from 15–18% to 7–11%), the crystallinity of the rPET matrix materials over the entire range is about 3% higher than that of the oPET matrix materials. The higher tendency of rPET to crystallize can be explained by the higher ordering of shorter molecular chains [8,49]. The abrupt decrease in crystallinity and melting temperature due to EBA-GMA in the case of oPET suggests more imperfect crystals formed due to longer chains [50].

Quasi-static mechanical properties were characterized by flexural tests. Figs. 8a and b show the change in flexural strength and

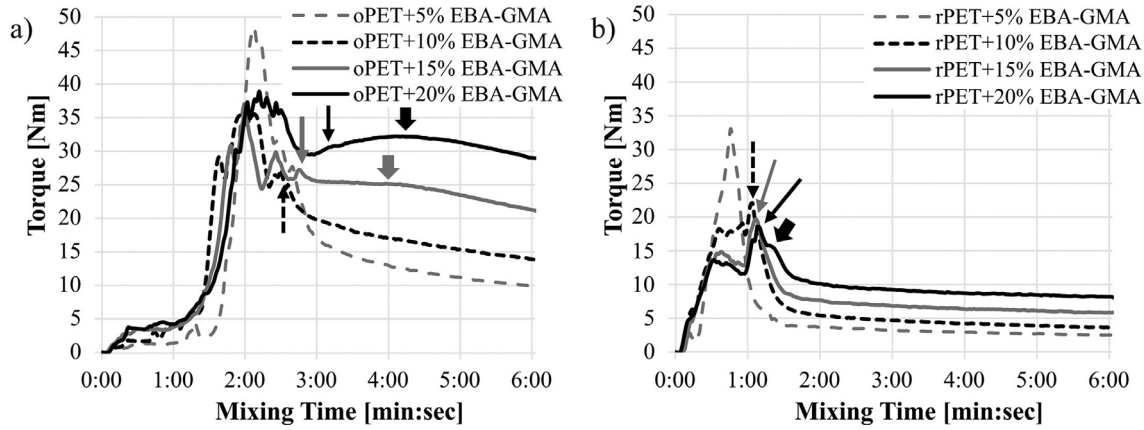

Fig. 5. Torque responses as a function of time recorded during melt mixing of the binary blends a) with oPET and b) with rPET (thin arrows point at peaks indicating compatibilization while thick arrows point at changes corresponding to crosslinking).

Table 1
Results of DSC measurements.

Major component	EBA-GMA content [%]	T_g [°C]	CRF_{CC} [%]	T_{CC} [°C]	CRF_M [%]	T_M [°C]	CRF_0 [%]
oPET	0	76.4	16.5	125.5	31.7	253.6	15.2
	5	74.2	11.2	125	22.5	248.7	11.3
	10	76.8	10.6	123.7	20.9	249.2	10.3
	15	75.4	9.2	123.3	18.8	249.1	9.6
	20	75.6	9.7	123.3	16.4	249.1	6.7
rPET	0	76.6	14.4	126	31.9	252.2	17.5
	5	77.2	11.6	124.5	26.9	251	15.3
	10	76.2	10.7	124.4	24.3	251	13.6
	15	74.5	10.3	123.3	21.7	250.1	11.4
	20	75.5	9.0	122.5	19.6	249.9	10.6

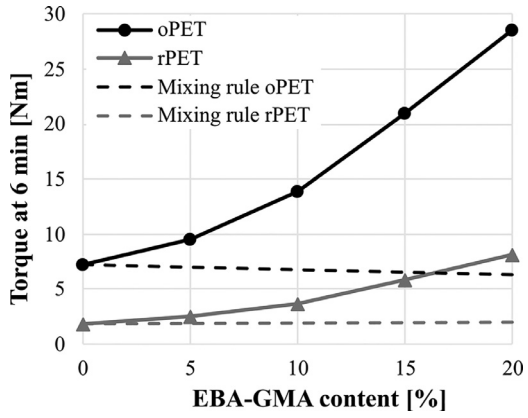

Fig. 6. Comparison of calculated and equilibrium torque values registered at 6 min as a function of EBA-GMA content.

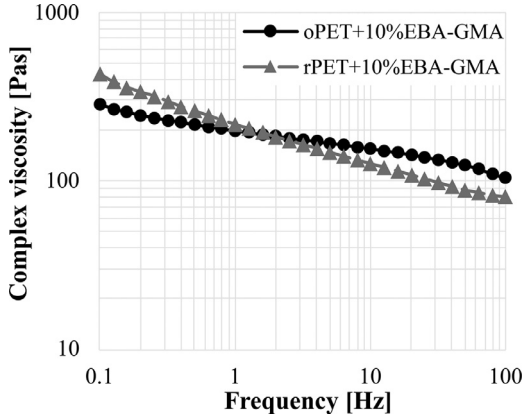

Fig. 7. Complex viscosity versus frequency for oPET + 10% EBA-GMA and rPET + 10% EBA-GMA blends (log-log scale).

modulus as a function of EBA-GMA content, respectively. In the case of both oPET and rPET matrices, the strength and stiffness decrease in a similar way as the proportion of the distributed component increases. It must be noted, however, that rapid increase in the Izod-impact strength of oPET is only observable at 20% EBA-GMA content, when the strength and stiffness are about 50% lower than those of 100% oPET. In the case of rPET, however, the Izod-impact strength increases sharply already at 10% EBA-GMA ratio, the strength and the stiffness at this composition are only about 25% lower than those of the 100% rPET material. This advantage of rPET based blends can be of key importance from the aspects of product development.

3.2. Reactive toughening of different PET grades

The influence of the molar mass of polymer matrix on the toughening efficiency of the reactive compatibilizer was investigated. For this purpose, oPET was subjected to multiple extrusion cycles (thus modelling mechanical recycling [11]) using an LTE 26–48 (Labtech Scientific, Thailand) twin-screw extruder to obtain PET grades differing in degradation state (molecular weight), as characterised by IV and GPC measurements (Table 2). During extrusion, zone temperatures between the hopper and the die were between 230 °C and 270 °C and the screw speed was 20 1/min. By this method, a 5-member series (including oPET and rPET) of PET grades were obtained to be analysed covering a wide IV range. To

Table 2
IV values, average molecular weight and polydispersity index (PDI) of PET grades obtained after different number of extrusion cycles.

Sample code	Number of extrusion cycles	IV [g/dl]	M_w [g/mol]	PDI
oPET		0.80 ± 0.02	27 400	2.71
rPET		0.56 ± 0.03	16 900	2.43
PET-1x	1	0.74 ± 0.02	25 200	2.80
PET-2x	2	0.64 ± 0.02	21 500	2.56
PET-3x	3	0.48 ± 0.02	14 850	2.38

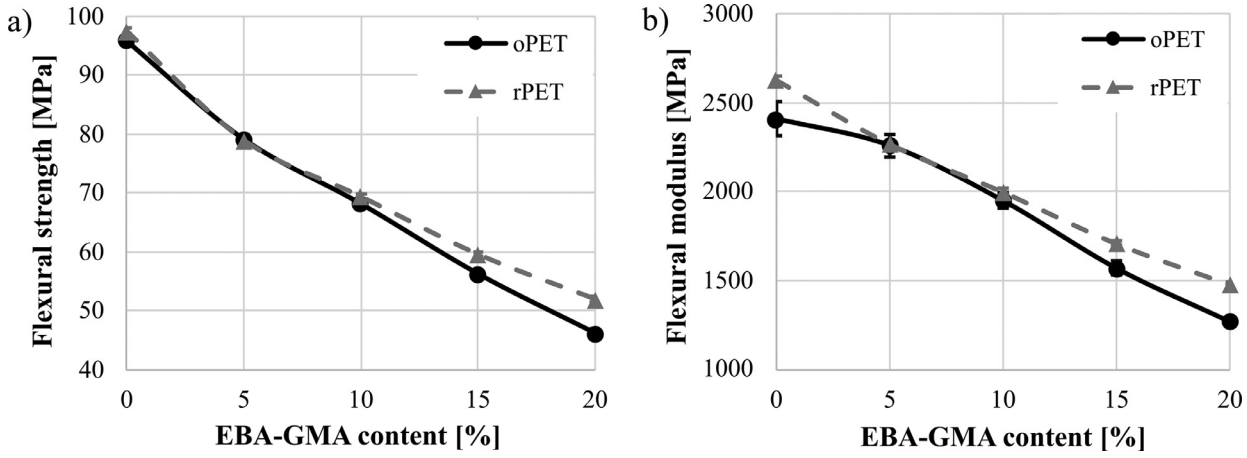

Fig. 8. Results of the flexural test a) flexural strength vs. EBA-GMA content; b) flexural modulus vs. EBA-GMA content.

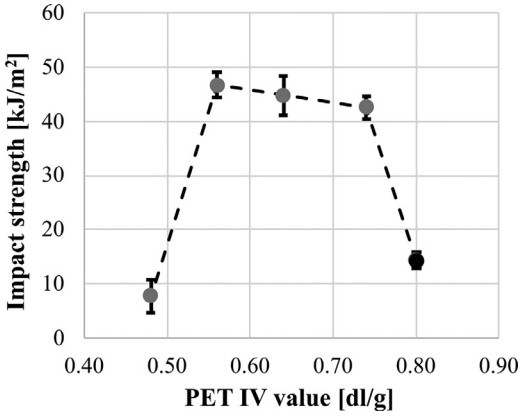

Fig. 9. Double-notched Izod impact strength of different PET grades with 15% EBA-GMA content.

examine the toughening efficiency of EBA-GMA in the different PET grades, a constant weight fraction of 15 wt% compatibilizer was selected for the binary blends. Namely, at this ratio only moderate improvement in the Izod impact strength was observed in oPET matrix, while a sharp increase was measured in rPET with IV of 0.56 g/dl (see Fig 1). (Compounding and injection moulding were carried out as described in the Materials end Methods Section.)

In Fig. 9, the double-notched Izod impact strength of the 15% EBA-GMA containing binary blends is presented as a function of IV value of the used PET grades. It can be seen that in the case of oPET and PET-3 × 15 wt% EBA-GMA does not suffice to reach outstanding impact resistance. However, in the case of PET grades with IV values ranging between 0.56 and 0.72 g/dl Izod impact strength values higher than 40 kJ/m^2 were measured. The critical molar mass value (M_c) for PET to reach the transition from ductile to brittle behaviour is considered to be around 17 000 g/mol [15]. Therefore, it is proposed that the inadequate toughening performance of EBA-GMA in PET-3x matrix is due to the insufficient entanglement density of this highly degraded grade (with IV value of 0.48 g/dl), which renders the low-molecular-weight polymer incapable of absorbing energy by shear yielding to make the toughening successful [51,52]. At high molecular weight (at IV of 0.80 g/dl or higher), the PET/EBA-GMA compatibilization reaction is believed to be suppressed by the limited number of reactive functional groups and lower proportion of the more reactive carboxyl end groups, providing more opportunity to the competitive crosslinking reactions to take place and thus hindering stable dispersion of the rubber-like component.

It has to be highlighted that the IV values of real PET recyclates originating from bottle- or sheet production typically fall in the favourable range of 0.56–0.72 dl/g where already 15% EBA-GMA outstandingly increases the notched impact resistance. Consequently, high impact resistance products can be manufactured from PET waste, independently from its actual quality (degradation state), with noticeably reduced amount of reactive toughening agent than necessitated in original PET. This finding could serve as a new and economic driving force for the production of high-quality products from secondary materials.

3.3. Optimisation of the recyclate content of PET/EBA-GMA systems

Although EBA-GMA was found to be especially efficient in increasing the impact resistance of PET grades with IV values ranging between 0.56 and 0.72 dl/g, the high recyclate content could be a limitation in several fields of application [53]. For example, when waste PET is used as raw material then the colourability and gloss value of the material generally decreases, and the probability of other potential impurities increases which may even dissolve from the products. In case of possible utilization in the food industry, the recyclate must be subjected to a 'super-cleaning' process [54] to meet the requirements, which can significantly increase production costs if a higher proportion of waste is used. Nevertheless, the incorporation of recycled polymer fraction was found to be advantageous in many studies, various material properties such as tensile strength in wood-HDPE- composites [55]; shrink-

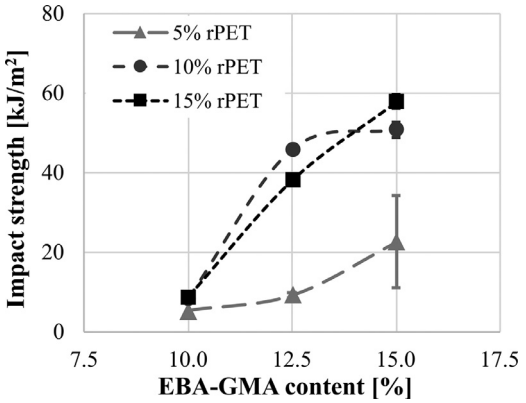

Fig. 10. Double notched Izod impact strength of the three-component blends.

Table 3
Composition of the three-component blends.

oPET content [%]	rPET content [%]	EBA-GMA content [%]
85.0	5.0	10.0
82.5	5.0	12.5
80.0	5.0	15.0
80.0	10.0	10.0
77.5	10.0	12.5
75.0	10.0	15.0
75.0	15.0	10.0
72.5	15.0	12.5
70.0	15.0	15.0

age in virgin/recycled ABS blends [56]; or Charpy-impact strength in PP/PET blends [53] improved due to the use of recyclates.

Based on these considerations, samples with reduced rPET contents were examined hereinafter, i.e. the characteristics of PET/EBA-GMA blends were investigated, where the oPET matrix was only partially replaced by rPET (with IV value of 0.56 g/dl). To optimise the composition of the toughening system, three-component blends with EBA-GMA contents of 10, 12.5 and 15% were prepared besides varying the ratio of rPET in the range of 5 to 15%. Possible errors due to the compounding order were eliminated by randomizing the production order. The compositions of the obtained three-component blends are given in Table 3.

The impact strength of the sample series was analysed by double-notched Izod impact tests; the results of which are presented in Fig. 10. In 100% oPET matrix, up to 15% EBA-GMA content, only a moderate increase of the impact strength was measured (see Fig. 2). It was found that 5% rPET only slightly improves these results. However, the addition of 10 or 15% rPET to the oPET matrix causes a sharp increase in the impact strength; at 15% EBA-GMA content notched Izod impact strength higher than 50 kJ/m^2 was reached. It can also be seen from the diagram that with the addition of rPET, outstanding impact strength can be achieved even with elastomer contents lower than 15%. While 20% EBA-GMA is required in the oPET matrix to provide prominent impact strength, with 10% rPET added to the system 12.5% EBA-GMA is sufficient to achieve a similar result. This result is extremely significant from an economic point of view, as outstanding impact strength is ensured while economizing almost half of the elastomer additive, and all this is achieved by using the valueless (unmarketable), highly degraded secondary PET fraction.

Flexural tests were performed to investigate the evolution of the mechanical properties, other than impact resistance, when oPET is partly replaced by rPET. The obtained flexural strength and modulus values of the sample series are shown in Fig. 11a and b, respectively. The diagrams show the favourable case that the strength and stiffness are mainly a function of the EBA-GMA content, decreasing linearly with its increasing ratio. Apparently, the small proportion of rPET does not have a significant influence on these properties; it only slightly increases modulus at lower EBA-GMA contents.

Based on the flexural test results, there are further benefits accompanied to our finding that reduced quantity of EBA-GMA is needed to provide prominent impact strength in rPET containing matrix. Namely, at reduced proportion of EBA-GMA, the strength and stiffness of the blends can be maintained at a higher level. Compared to the 20% EBA-GMA containing oPET blend, by 37% increased flexural strength and by 48% increased flexural modulus can be ensured with the 10% rPET containing blend (oPET/rPET/EBA-GMA: 77.5/10.0/12.5) of reduced (12.5%) EBA-GMA content but with comparable notched impact strength.

Then, the applicability of other PET grades, differing in degradation state (IV values and M_w see in Table 2), as potential toughness improving mediators were investigated. The toughening efficiency of 15% EBA-GMA was examined besides adding 10% of different PET grades while keeping the overall oPET content of 75%. The Izod impact strength of the thus produced three-component blends is presented in Fig. 12. It can be seen that the impact strength of the two-component blend (14 kJ/m^2) noticeably increases to values above 35 kJ/m^2 just by the addition of 10% of decreased-molecular-weight PET. The improvement in impact strength appears to be in-

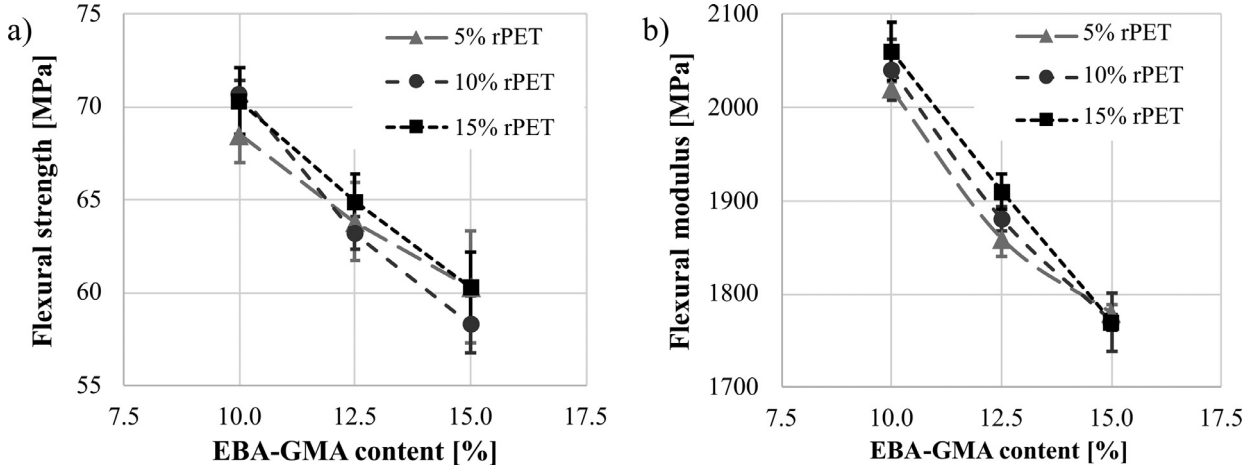

Fig. 11. Bending test results of the three-component blends a) flexural strength vs. EBA-GMA content; b) flexural modulus vs. EBA-GMA content.

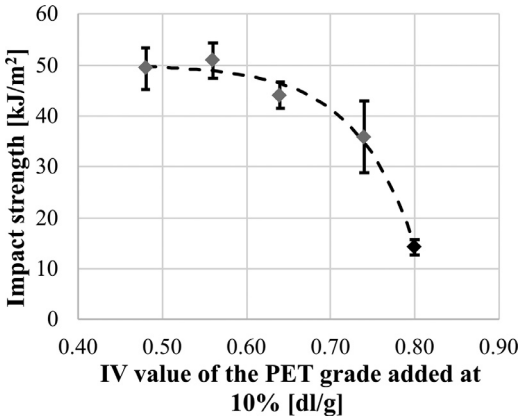

Fig. 12. Double-notched Izod impact strength as a function of the PET additive's IV value (in the case of 15% EBA-GMA and 10% of recycled PET additive content).

dependent of the quality of the added decreased-molecular-weight PET grade, at least below a certain IV value of 0.74 g/dl. This is a key finding from a practical point of view, as it means that product quality is not affected by fluctuations in waste quality.

4. Conclusion

In our research, we have found that the efficiency of the EBA-GMA type reactive toughening agent can be greatly improved by the correct choice of the PET matrix. The use of rPET, due to the available larger number of reactive functional end groups and increased mobility of the decreased-molecular-weight chains, multiplies the impact strength of the product compared to that of oPET with identical EBA-GMA content. In other words, 50% less reactive toughening agent (10% EBA-GMA) is sufficient to achieve comparable impact strength using rPET instead of oPET. The significantly increased impact resistance is ascribed to the formation of a Toughening Enhancer Interphase (TEI) consisting of reactive shorter chain rPET macromolecules.

Based on systematic experiments conducted with "artificial" PET waste fractions, i.e. PET grades differing in degradation state as characterized by IV values and M_w, the following conclusions were drawn:

- In 100% recycled PET matrix, with IV values between 0.56 and 0.74 dl/g, notched impact strength higher than 40 kJ/m^2 can be reached with a reduced amount (10%) of EBA-GMA.
- In case of original PET matrix with 12.5% EBA-GMA content, the addition of as low as 10% recyclate with IV value lower than 0.74 dl/g increases the notched impact strength from 9 kJ/m^2 to higher than 40 kJ/m^2.

It is proposed that during extrusion, when all components begin to melt, the shorter chains of the recyclate are able to react with the functional groups of EBA-GMA, being especially reactive at the high processing temperature of PET, faster and to a greater extent. The simultaneous compatibilization and fragmentation of the elastomer particles are of key importance in the creation of large interfaces and successful toughening (Fig. 13). Thereafter, through the unreacted epoxy groups of the elastomer crosslinking reactions take place in the extruder that stabilizes the particle size. However, if there are no short chains present in the system, the process of attachment of the longer and less mobile PET chains to the EBA-GMA particles will not be able to compete with the crosslinking reaction within the EBA-GMA particles hindering their fragmentation and thus resulting in larger particles.

Consequently, to ensure stable dispersion of the elastomer phase, the compatibilization through carboxyl/epoxide reaction must precede the hydroxyl/epoxide crosslinking (Fig. 1). The increased ratio of carboxyl end groups and lower viscosity of the degraded PET chains contribute to the prevalence of compatibilization over crosslinking. Below a certain molecular weight, however, the insufficient entanglement density of the recycled matrix encumbers the effective energy absorption by shear yielding. Therefore, the highly degraded waste fractions (IV lower than 0.56 dl/g) are suggested to be applied as additives in 10% dosage for successful enhancement of the toughening efficiency of EBA-GMA and without compromising other (mechanical, aesthetic, safety) properties. The significantly improved material properties render the impact-resistant PET-based materials suitable for even injection moulding applications. Besides, this way of utilisation of PET recyclate, even the unmarketable highly degraded fractions, can give a new driving force in PET recycling.

The application of low-molecular-weight polymer fractions to enhance the efficiency of reactive additives could be successfully exploited in other polymeric systems, such as in PBT or PLA matrix, and/or in combination with other reactive modifiers as well (patent pending [57]).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Katalin Bocz: Conceptualization, Methodology, Writing - original draft, Supervision. **Ferenc Ronkay:** Conceptualization, Methodology, Writing - original draft. **Kata Enikő Decsov:** Investigation, Visualization. **Béla Molnár:** Investigation. **György Marosi:** Supervision, Writing - review & editing.

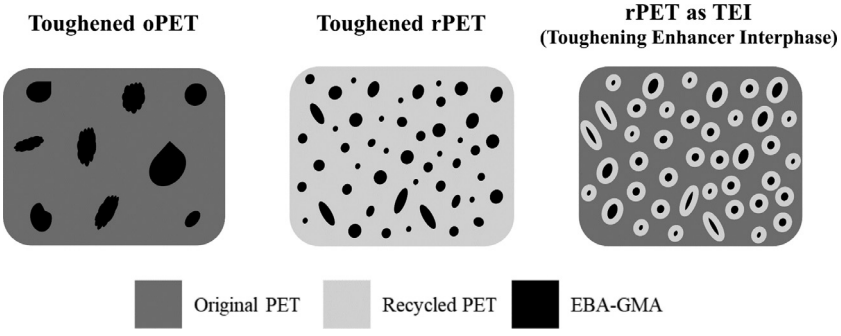

Fig. 13. Schematic phase morphologies of the PET/EBA-GMA systems.

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